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<p>14. ABSTRACT Unlike supported particles of larger size or extended solid surfaces, size-selected small metal clusters (in particular gold) adsorbed at specific sites of a support material (e.g. oxygen vacancies in the case of a MgO(100) surface) exhibit unique properties that originate from the highly reduced dimensions of the individual metal aggregates. Our first-principles electronic structure and MD simulations, in conjunction with experiments, show that these properties underlie the remarkable newly found catalytic activity of small gold clusters, and they include: (i) structural dynamical fluxionality that exhibits itself through the propensity of small clusters to transform in the course of chemical reactions between various energetically accessible structural isomers, thus enhancing the rates for overcoming reaction barriers. (ii) quantum size effects that are reflected in size-dependent characteristics of the electronic energy-level spectra of small gold clusters, as well as in charging of the clusters by the support. (iii) impurity-doping effects that allow modification and control of the electronic structure and consequent chemical reactivity of small supported clusters. </p>				
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HETEROGENEOUS CATALYSIS AND METAL / METAL-OXIDE INTERFACES

Grant Number: F49620 - 00 - 1 - 0046

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I. Summary of Research Activities

The research performed under this grant focused on 3 main topics:

1. Studies of the atomic and electronic structure of neutral and anionic small gold clusters, and other coinage metal clusters.
2. Investigations of catalysis of the oxidation of CO by small gold, and other coinage metal, clusters supported on MgO(100).
3. Investigations of gas-phase reactions of oxygen and carbon monoxide molecules with small (anionic) gold clusters, and the catalytic activity of such clusters for CO oxidation.

1. Gold, and other coinage metal, clusters and their anions

(i) Hannu Hakkinen and Uzi Landman, “ Gold Clusters (Au_N , $2 \leq N \leq 10$) and their Anions”, Phys. Rev B 62, R2287 (2000).

Nanoscale gold particles and compounds play an important role in colloidal chemistry, medical science, and catalysis. In light of the above and a recent discovery of extreme size sensitivity of catalytic activity of supported gold clusters with up to 20 atoms (see part 1 of this progress report), as well as early observations of reactivity of gas-phase cluster anions, there is an urgent need to understand structures and bonding in small neutral and anionic gold clusters.

In the above paper we reported on systematic density-functional theory (DFT) investigations of the atomic and electronic structures of gold

clusters, Au_N , and their anions, Au_N^{-2} , with $2 \leq N \leq 10$. The vertical electron detachment energies (vDE) of the ground-state anions were found to be in very good agreement with photoelectron spectroscopy (PES) data, and their structural sensitivity was illustrated through comparison between the values calculated for the ground-state structures and those corresponding to higher-energy isomers. The photo-fragmentation patterns of the cluster anions exhibit a dependence on cluster size with asymmetric fragmentation favored for all sizes, and the interplay between such processes and electron photodetachment is correlated with results obtained via laser experiments for Au_3^- .

In these studies we used the Born-Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD method, employing scalar-relativistic *ab initio* pseudopotentials for the $5d^{10} 6s^1$ valence electrons of gold, and the recent generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof is used for the exchange-correlation potential. For comparison, some calculations for $\text{Au}_2 - \text{Au}_4$ clusters were repeated without the GGA by using the LSD parametrization by Vosko, Wilk, and Nusair. All the structures were fully optimized without any symmetry constraints, starting from a large number of initial candidate geometries. Interestingly, neutral clusters with up to seven atoms are found to be planar, and for the anions the transition to three dimensional clusters occurs for cluster anions with more than six atoms.

The results of our study, obtained through state-of-the-art LSD-GGA calculations, give insights into the systematics of the evolution of the geometric and electronic structures of gold clusters. The vDEs of the anionic clusters exhibit a strong structural sensitivity, and the remarkable agreement between the values calculated for the optimal cluster geometries

and the measured ones lends further support to our structural assignments. Using these results, as well as the energetics of fragmentation of the anionic clusters, we predict a planar triangular D_{3h} geometry for the much studied Au_6 cluster, and corroborate the interpretation of laser experiments on Au_3 cluster involving photofragmentation of the cluster and subsequent electron detachment from the charged fragments.

Finally, we comment that the low vDEs for Au_{2N} (with N larger or equal then 1 and smaller or equal to 5), associated with large HOMO-LUMO gap values of the corresponding neutral clusters, with their affinity levels lying above the antibonding Π^* LUMO of O_2 , make charge transfer from these clusters to the adsorbed molecule energetically favorable resulting in weakening of the interoxygen bond and stronger binding to the cluster. This observation correlates with the measured selective reactivity of gas-phase Au_{2N} clusters with O_2 , and with recent experimental and theoretical observations pertaining to the low-temperature catalytic oxidation of CO by Au_N ($8 \leq N \leq 20$) clusters adsorbed on $MgO(001)$ surfaces. Indeed, for $Au_8/MgO(001)$ (with and without surface oxygen vacancies) our LSD calculations have shown (see part 1 of this report) partial charging of the supported cluster, leading to activation of adsorbed O_2 which catalyses the CO oxidation producing CO_2 at temperatures as low as 140 K.

(ii) H. Hakkinen, M. Moseler, U. Landman, "Bonding in Cu, Ag, and Au Clusters: Trends and Surprises", Phys. Rev. Lett. 89, 033401 (2002).

The atomic electronic structure of Cu, Ag, and Au, featuring a filled d-shell and a singly occupied s-shell [$nd^{10}(n+1)s^1$, with $n=3,4$ and 5 for Cu, Ag, and Au], suggests that the properties of these coinage metals could be treated to first approximation within a "simple metal" framework -- that is,

as s^1 -electron systems perturbed, with increasing strength from Cu to Au, by the underlying filled d-shell. However, the above view may be oversimplified since this series contains Au which exhibits very strong relativistic effects.

we have shown through an extensive density functional study, focusing on Cu_7^- , Ag_7^- , and Au_7^- , that relativistic effects on bonding and structures in small gold clusters lead to quite remarkable results. In particular, the structures of the ground state and the close-lying first isomer of Au_7^- are found to be planar, separated by a large energy gap (0.47 eV, equivalent to an internal vibrational temperature of 730 K) from the lowest-lying 3D isomer. Furthermore, the propensity of anionic gold clusters to favor planar structures continues up to surprisingly large sizes, at least up to 13 atoms. This trend correlates with a relativistically-enhanced stronger sd hybridization and d-d interaction in gold than in Ag and Cu, where for the latter elements the 2D \rightarrow 3D structural transition occurs for smaller clusters.

The electronic and geometric structures (optimized without any symmetry constraints) were obtained through Born-Oppenheimer density functional calculations employing norm-conserving scalar-relativistic pseudopotentials and including self-consistent gradient corrections (PBE-GGA).

Finally, we note that our calculations predict that the tendency of Au_N^- clusters to prefer planar structures extends to surprisingly large sizes; that is, our results indicate that planar structures are energetically favorable up to at least $N=13$, correlating with recent measurements and related quantum-chemical calculations. This unique behavior, that has been shown here to be an added manifestation of the strong relativistic effects in gold, is

likely to influence the gas-phase reactivity and catalytic activity of small gold clusters, e.g. with O₂ and CO.

2. Nanoscale Catalysis by supported metal clusters

(i) A. Sanchez, S. Abbet, A. U. Heiz, W.-D. Schneider, H. Hakkinen, R. N. Barnett, and U. Landman "When Gold is not Noble: Nanoscale Gold Catalysts", *J. Phys. Chem. A* **103**, 9573 (1999).

Investigations of reactions heterogeneously catalyzed by metals and alloys are a major area of research endeavors. In our studies we focused on a class of catalysts which led recently to remarkable and rather surprising findings. In contrast to the inert nature of gold as bulk material, nanosize particles of gold supported on various oxides, as well as two-monolayer-thick gold islands of up to 4 nm diameter on titania, were found to exhibit an enhanced catalytic activity, in particular for the low-temperature oxidation of CO. While the novel heterogeneous catalysis by nanosize gold aggregates supported on oxides is of great significance in current and future environmental, sensor, and chemical technologies, the processes underlying the catalytic activity of gold in reduced dimensions and the reaction mechanisms are not yet understood.

In this joint experimental and theoretical study we addressed these issues through investigations of the low-temperature combustion of CO on size-selected gold clusters, Au_n (with n up to 20), supported on defect-poor and defect-rich MgO (100) films, demonstrating the size dependence of the activity of nanoscale gold clusters, with Au₈ found to be the smallest size to catalyze the reaction. Our first-principles simulations revealed that charging of the cluster via (partial) electron transfer from the oxide support, as well as

the presence of oxygen- vacancy (F-center) defects in the substrate, play an essential role in the activation of nanosize gold model catalysts.

To gain insights into the physico-chemical nature of the catalytic activity of ultra-fine supported gold clusters, detailed investigations of the CO oxidation by O₂ on mass selected Au_n (n = 8, 13, 15 and 20) particles deposited via “soft-landing”ⁱ on the surface of MgO (100) films grown on Mo (100), were performed by W. D. Schneider, U. Heiz and their associates at the Institut de Physique Experimentale, in the University of Lausanne. Using temperature programmed reaction (TPR) and Fourier Transform Infrared (FTIR) the oxidation reaction was investigated under UHV conditions. (Comparative studies were performed also for Pt_n clusters of the same sizes.) Isotopic labeling (i.e., ¹⁸O₂ and ¹³C¹⁶O) was used to verify that the carbon dioxide product (i.e., ¹³C¹⁸O¹⁶O) did not originate from the MgO support. In these experiments the model catalyst was first exposed to O₂ at 90 K and subsequently to CO. The main results of these studies include: (i) at low temperature the clusters of all sizes (up to 20 atoms) oxidize CO at around 160 K; (ii) at higher temperature each cluster size reveals a distinctly different oxidation temperature e.g., 240 K for Au₈ and 500 K for Au₂₀; (iii) The catalytic activity expressed by the number of CO₂ produced per cluster, results in a constant reactivity of one CO₂ molecule per gold cluster, for all the Au_n cluster sizes (which is in contrast to Pt_n where an abrupt increase in the reactivity is observed between Pt₁₃ and Pt₁₅); and (iv) The Au₈/MgO model catalyst system is stable up to at least 350 K. These results, as well as measured vibrational frequencies (for example CO on clean MgO (001), on Au₈/MgO (without O₂), and on Au₈/MgO during the course of reaction at various temperatures), and further experiments developed during our collaborative investigations with the Lausanne researchers (such as

“titration” of the MgO surface by NO for detection of oxygen vacancies, see below), form a data base for our theoretical studies.

Our theoretical investigations investigation are based on the BO-LSD-MD method (developed in our group, see R. N. Barnett and U. Landman, Phys. Rev. B 48, 2081 (1993)), with the use of non-local norm-conserving pseudopotentials (scalar-relativistic for gold with 11 valence electrons per atom). The method which we developed (whose formulation is described in detail in the Phys. Rev. B paper cited above⁰) employs a dual-space representation (momentum and real space) using fast-Fourier transform (FFT) grids. It is uniquely suited for calculations and simulations of (finite-size) charged systems or systems where large multipole moments develop, since we developed the method such that no replication (using periodic boundary conditions) of the ionic system is done. It is worth noting here that the BO-LSD-MD computer-codes have been recently rewritten and optimized by us for massive parallel computations, allowing treatment of rather complex (and large) systems.

In general, two methodologies are used in first-principles calculations involving the surfaces of ionic systems; a supercell method using finite thickness slabs and cluster or embedded-cluster (EC) methods. Both methods have certain (documented) advantages and disadvantages. In particular, due to the long-range nature of ionic (and multi-polar) interactions, the thickness of the slab (for the metal-oxide support) and that of the empty space regions when using a super-cell method may need to be very large, in order to achieve convergence (although in certain studies, it had been argued that some quantities, especially those involving differences between total energies, converge rapidly with respect to the slab and empty space thickness). In comparative calculations which we performed for MgO (100)

using the EC method we obtained structural and energetic results in very good correspondence with experiments; in these calculations a cluster of 54 Mg atoms and 54 oxygen atoms (with their valence electrons treated self-consistently) was embedded in the field of 2006 point charges (modeling the host MgO lattice), with the magnesiums which are nearest-neighbors to the cluster oxygens described via the full non-local pseudopotential (without the valence electrons). The size of the top surface of the MgO (100) cluster described above (7x7 ionic sites) allows for accurate calculations of adsorbed gold clusters of up to 20 atoms (as verified through comparative total energy calculations for larger representations of the MgO surface).

In our theoretical study we determined first the equilibrium geometries of adsorption of Au_8 clusters on Mg(100) with and without the presence of an oxygen vacancy (F-center), and have discovered that in the adsorbed state the gold cluster is charged by about 0.5e. Subsequently, we have investigated the adsorption of molecular oxygen and CO on the cluster, and found activation of the adsorbed dioxygen that is manifested by elongation of the inter-oxygen bond length of the adsorbed species. Furthermore, we have identified both an Eley-Rideal barrier-less mechanism for the production of CO_2 (through the reaction of an adsorbed activated oxygen molecule with a gas-phase CO molecule) and Langmuir-Hinshelwood (LH) type reactions between the activated oxygen molecule and CO, both adsorbed on the cluster. The LH reaction pathways involve activation barriers, depending on the adsorption site of the oxygen molecule, with the activation energy corresponding to the molecule adsorbed on top of the cluster being significantly smaller than the case where the oxygen molecule is adsorbed at the interface between the supported gold cluster and the MgO(100) surface; the barrier for the latter reaction is smaller when the

cluster is residing in the vicinity of an F-center of the substrate. These results were shown to correlate well with the trends found experimentally.

(ii) Structural, electronic, and impurity-doping effects in nanoscale chemistry: Supported gold nanoclusters

Metal clusters exhibit unique size-dependent physical and chemical properties that differ from those of bulk materials. While inert as a bulk material, gold nanoparticles and clusters have attracted lately considerable interest as active catalysts for a number of technologically relevant reactions. Unlike supported particles of larger size or extended solid surfaces, size-selected small metal clusters adsorbed at specific sites of a support material (e.g. oxygen vacancies in the case of a MgO(100) surface) exhibit unique properties that originate from the highly reduced dimensions of the individual metal aggregates. These properties underlie the remarkable newly found catalytic activity of small gold clusters, and they include:

(i) structural dynamical fluxionality that exhibits itself through the propensity of small clusters to transform in the course of chemical reactions between various energetically accessible structural isomers, thus enhancing the rates for overcoming reaction barriers.

(ii) quantum size effects that are reflected in size-dependent characteristics of the electronic energy-level spectra of small gold clusters, as well as in charging of the clusters by the support.

(iii) impurity-doping effects that allow modification and control of the electronic structure and consequent chemical reactivity of small

supported clusters, through incorporation of judiciously chosen impurity atoms in otherwise inert clusters.

Our studies focused on gaining fundamental insights into the above size-dependent “nanocatalytic factors”, and on illustrations, through joint experimental and theoretical investigations, of the manner in which such fundamental understanding may guide the design and atomic-scale modifications of nanocatalysts.

Recently (see section 2(i) of this report), a set of model catalysts have been prepared via soft-landing of mass-selected small gas-phase Au_n and Au_nSr cluster ions onto well-characterized $\text{MgO}(100)$ thin films. These substrate films contained a small concentration (typically 2 % ML) of oxygen vacancies (surface F-centers, FC), that act as strong trapping sites for the clusters at low temperatures. Temperature programmed reaction (TPR) measurements of CO oxidation ($\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$) have shown that the smallest gold cluster that catalyzes the reaction is Au_8 . Furthermore, it has been found that while Au_4 is catalytically inert the doped cluster Au_3Sr is active. These findings, in conjunction with first-principles theoretical simulations, have revealed that underlying the aforementioned remarkable chemical size-sensitivity is the nature of bonding and activation of molecular oxygen by these nanocluster catalysts.

The atomic structure and the electronic spectra of gold cluster model catalysts were studied by extensive first-principles simulations. Gold clusters in the size range of 3-8 atoms bind to the $\text{MgO}(\text{FC})$ surface quite strongly (calculated binding energy of 2.65 eV to 4.06 eV), and their binding is significantly enhanced (typically by about 2 eV) due to the F-center defects.

These high binding energies and the “anchoring” effect by the F-centers correlate well with the observed thermal stability of the supported clusters in the TPR experiments. Another important finding pertains to the charge state of the adsorbed clusters – in particular, our calculations predict that the interaction with the surface is accompanied by charge transfer of 0.5e, 0.3e, and 0.3e to the adsorbed Au_8 , Au_4 and Au_3Sr clusters, respectively.

Binding and activation of molecular O_2 by the model catalyst are necessary elementary steps in the CO oxidation process, and thus understanding the structural, dynamical, electronic and compositional factors that govern these processes are key to elucidation of the observed size-dependent activity of the $\text{Au}_n/\text{MgO}(\text{FC})$ model catalysts. Indeed, our first-principles simulations show that the binding energy of O_2 to the supported Au_n clusters and the degree of O-O bond activation are strongly dependent on the cluster size (see below). In contrast, the adsorption energy of CO to the supported clusters is relatively insensitive to the cluster size, and it is higher than that of oxygen (0.7-1.0 eV per CO molecule, depending on coverage). Consequently, we focused on the adsorption and activation of O_2 by the supported gold nanoclusters, and illustrated the aforementioned nanocatalytic factors that govern this key reaction step.

(i) Structural Dynamical Fluxionality: The capability of small clusters to exhibit several structural forms (isomers) of comparable energies, and to interconvert between such isomers at finite temperature, is one of the hallmarks of cluster science. This unique structural variability may influence the chemical reactivity of nano-catalytic systems in two main ways. First, at finite temperature, the model catalyst (and in particular the cluster

component) will form an equilibrium ensemble of coexisting structural configurations, with various isomers exhibiting different chemical reactivities. Second, and most importantly, is the structural dynamic fluxionality of clusters in the course of reactions that expresses itself in the ability of a given structural isomer to dynamically adapt its structure such as to allow the reaction to evolve on the most favorable free-energy path.

(ii) Electronic Size Effects: Understanding the size-dependent electronic structure of the $\text{Au}_N/\text{MgO}(\text{FC})$ model catalysts, which is fundamental for elucidation of their atom-by-atom controlled reactivity, is facilitated by analysis of the spectra of the local density of electronic states (LDOS) projected on the oxygen molecule and on the metal cluster; a similar analysis is often employed in the context of the interaction of adsorbates with extended surfaces. Examination of the LDOS projected on the O_2 molecule which is adsorbed at the periphery site of the more reactive isomer of the $\text{Au}_8/\text{MgO}(\text{FC})$ model catalyst, reveals that all the prominent peaks of the LDOS spectrum can be unambiguously assigned to orbitals of (free) molecular oxygen origins. In addition, these states overlap with the entire d-band of the Au_8 cluster in the range of $-7 \text{ eV} \leq E \leq E_F$, where E_F is the Fermi energy. Bonding of the oxygen molecule to the gold octamer involves mainly hybridization of the 5σ , $1\pi_{\parallel}$, and $1\pi_{\perp}$ oxygen states with the gold d-band. Most importantly, the full spin-manifold of the antibonding $2\pi^*$ states of O_2 is located below E_F , resulting in strong activation of the O_2 molecule through occupation of the antibonding orbitals. This leads to weakening of the O-O bond that is reflected in a significant increase of its length (1.43 Å) compared to that of the free molecule (1.25 Å). Accompanying the activation process is a change in the spin state of the

molecule from a triplet state in the gas phase to a peroxyo-like adsorbed state with a zero net spin.

A drastically different scenario is found for the interaction of O₂ with the smaller gold cluster, Au₄/MgO(FC), where molecular oxygen adsorbs in an “on-top” configuration, with one of the oxygen atoms binding to a single gold atom. This system exhibits rather weak binding of the molecule to the metal cluster (0.18 eV), an almost unperturbed O-O bond length (1.28 Å), and a spin-splitting of the oxygen-projected LDOS spectrum. The weak binding is attributed to the narrower d-band of the adsorbed Au₄ cluster compared to that of Au₈ (see Figs. 1B and 1D), with a consequent lack of overlap between the states at the bottom of the d-band of the gold cluster and the molecular oxygen states with energies E < -5 eV. Moreover, the spin-down antibonding $2\pi_{\perp}^*$ and $2\pi_{\parallel}^*$ orbitals of the adsorbed oxygen molecule are located now above E_F (unlike the case of the larger cluster) which results in no activation of the molecule by the adsorbed Au₄ cluster.

(iii) Impurity-doping Effects: Finally, we address the possibility of enhancing the catalytic activity of a nanocluster by designed incorporation (doping) of an impurity, demonstrated here by the catalyzed oxidation of CO on Au₃Sr/MgO(FC). Inspection of the LDOS spectra projected onto the oxygen molecule, the Sr atom, and the Au₃ part of the metal cluster, shows that doping by a single impurity atom changes significantly the bonding and activation of O₂ compared to the pure gold tetramer, Au₄, case; the bonding of O₂ is mainly to the strontium atom of the Au₃Sr cluster, and it is characterized by a substantially higher adsorption energy (1.94 eV compared to 0.18 eV) and a significant activation of the O-O bond that is

reflected in an increased bond length of 1.37 Å. This activation is due to occupation of the spin-down $2\pi_{\perp}^*$ oxygen orbital, resulting in a superoxo-like state of the adsorbate. Bonding of the oxygen over E_F molecule to $\text{Au}_3\text{Sr}/\text{MgO}(\text{FC})$ occurs via resonances formed between the Sr states in the energy intervals (5 – 6) eV and (0 – 1) eV below E_F , with the spin-up $1\pi_{\parallel}$ and $2\pi_{\perp}^*$ states, as well as with the spin-down $1\pi_{\perp}$ and $2\pi_{\perp}^*$ orbitals, of the adsorbed activated O_2 .

In summary, we identified and illustrated here some of the key physical factors that underlie the chemical activity of supported nanoclusters, with a particular focus on the adsorption and activation step of molecular oxygen, that is essential for the oxidation of CO on supported gold model nanocatalysts. First, the metal-oxide support, and in particular surface oxygen vacancy sites, were found to play a dominant role in anchoring the metal clusters, and in activating the clusters via (partial) charge-transfer. Second, the structural dynamical fluxionality of the model catalyst (and in particular the isomerization propensity of the metal cluster component) is predicted to enable and promote binding and activation of the reactants and to allow propagation of the catalyzed reaction along an optimal path through concurrent structural rearrangements of the model catalyst. Third, observed size-dependent patterns pertaining to activation of the reactants by the model catalyst and the promotion of consequent reactions, are found to be correlated with subtle features in the electronic structure of the catalyst (in particular the width and positioning of the d-band of the model gold catalyst) that govern in turn the formation of bonding resonances between the molecular states of the reactants and the electronic states of the supported cluster. Finally, we have shown that catalytically inert clusters

(e.g., supported gold tetramers) can be activated by substitutional doping with impurity atoms (e.g. Sr) that strongly bind and activate the reactants. These results may form guiding principles for further endeavors in the growing field of nanocatalysis, aiming at atomic-scale design of nanocatalysts with desired chemical activity, specificity, and selectivity.

(iii) S. Abbet, U. Heiz, H. Häkkinen, and U. Landman, “CO Oxidation on a Single Pd Atom Supported on Magnesia”, Phys. Rev. Lett. 86, 5950 (2001).

We reported on studies of the oxidation of CO by a model catalyst consisting of single Pd atoms anchored on oxygen surface vacancies (F-centers, FCs) of a MgO(100) film. After low-temperature (90 K) coadsorption of O₂ and CO the formation of CO₂ was detected by temperature programmed-reaction (TPR) mass spectrometry in single heating- cycle experiments. *Ab initio* density-functional simulations were performed to identify relevant molecular precursors as well as to study the CO₂ formation mechanisms.

First, we verified that the clean MgO(100) thin films are inert for the oxidation reaction; i.e., no CO₂ was formed in a one-heating-cycle experiment after adsorbing O₂ and CO or vice versa. When Pd atoms are trapped on the FCs, preadsorption of oxygen and subsequent saturation by CO leads to the formation of carbon dioxide, with desorption peaks at 260 K and at around 500 K. The existence of two desorption peaks suggests the presence of two different reaction mechanisms. Note that when CO is preadsorbed prior to O₂ the oxidation reaction is suppressed, indicating CO poisoning.

The calculations were performed using the Born-Oppenheimer (BO) local spin-density (LSD) molecular dynamics method (BO-LSD-MD, see R.N. Barnett and U. Landman, *Phys. Rev. B* **48**, 2081, (1993)) with the generalized gradient approximation (GGA) and employing norm-conserving nonlocal scalar-relativistic (for the Pd atom) pseudopotentials. Such calculations yield accurate results pertaining to geometries, electronic structure, and charging effects of various neutral and charged coinage metal clusters and nanostructures [see work by our group in *Phys. Rev B* **62**, R2287 (2000); *Phys. Rev. Lett.*, **86**, 2545 (2001); *J. Phys. Chem. B* **104**, 9063 (2000)]. The magnesia surface was modeled by a finite region (“cluster”) of atoms, whose valence electrons are treated fully quantum mechanically (using the BO-LSD-MD), embedded in a large (2000 charges) point charge lattice, as described in our previous study of the Au_8/MgO model catalyst.

A single Pd atom binds strongly to the oxygen vacancy (binding energy of 3.31 eV), with a slight amount of charge (0.15 e) transferred to the adsorbed atom. In comparison, the binding energy of Pd atoms to terrace oxygen sites is only 1.16 eV. The enhanced binding to the FCs is also reflected in the corresponding bonding lengths of 1.65 and 2.17 Å for $\text{MgO}(\text{FC})\text{-Pd}$ and $\text{MgO}\text{-Pd}$, respectively. Binding of two CO molecules saturates the $\text{MgO}(\text{FC})\text{-Pd}$ system; occupying the $\text{MgO}(\text{FC})\text{-Pd}$ system with three CO molecules leads to spontaneous (barrierless) desorption of one of the molecules. In the most stable configuration the two CO molecules are inequivalent; one CO binds on top and the second adsorbs on the side of the Pd-atom, and the total binding energy of the two CO molecules is 1.62 eV.

An alternative symmetric adsorption configuration, with the two CO molecules adsorbing on opposing sides of the Pd atom, is less stable by 0.61 eV than the top-side one.

Our theoretical determination of two initial molecular complexes (precursors) adsorbed on MgO(100), Pd(CO)₂O₂, and PdCO₃CO, is supported by good agreement between the measured and calculated CO vibrational frequencies. The former complex is involved in the formation of CO₂ at 260 K, and the decomposition of the carbonate complex leads to CO₂ desorption at 500 K. Both reaction routes induce annealing of the surface FC and migration of the remaining Pd-CO unit to form larger Pd clusters.

Finally, we remark that the relative abundance of the two surface precursors, Pd(CO)₂O₂ and PdCO₃CO, underlying the above reaction mechanisms may be dominated by kinetic factors; e.g., formation of the carbonate complex, although energetically favorable, could be hindered by the requirement that the CO molecule will approach the preadsorbed side-O₂ rather than the Pd atom, as well as by a significant reaction barrier. Further studies of the low temperature formation of the carbonate complex, as well as efforts to identify such species (e.g., via HREELS), are warranted.

3. “Gas-Phase Catalytic Oxidation of CO by Au₂”, Hannu Hakkinen and Uzi Landman, , J. Am. Chem. Soc. (Communication) 123, 9704 (2001).

The chemical reactivity of the gold dimer anion towards oxygen and carbon monoxide was investigated by using density functional theory, the generalized gradient correction, and scalar-relativistic treatment of the gold

pseudopotential. In the energy-optimal configuration for Au_2O_2^- , oxygen is strongly and molecularly bound to gold (binding energy of 1.37 eV). The bonding involves occupation of the pi-antibonding orbital of the oxygen molecule by the anionic charge by 0.4 e (making the oxygen molecule superoxo-like), the rest of the charge (0.6 e) residing in the gold. The extra charge on the oxygen molecule activates slightly the molecular bond, stretching it to 1.35 Å (calculated equilibrium bond length for neutral oxygen is 1.25 Å). The vertical detachment energy of the molecularly bound gold-oxygen complex is 3.04 eV. The other possible binding configurations (involving molecular as well as dissociated states of oxygen) are at least 0.85 eV higher in energy having also rather different detachment energies. We suggest that an experimental determination of the electron detachment energy and photoelectron spectra of the Au_2O_2^- complex should prove most useful in verifying the bonding state of oxygen, where the definite answer (molecular vs. dissociated) is yet to be found in the flow-tube reactivity experiments.

We demonstrated a complete reaction cycle for CO oxidation catalyzed by the gold dimer anion, starting from the energy-optimal molecularly bound Au_2O_2^- complex, producing two CO_2 molecules, and yielding back the gold dimer anion. An important intermediate state involves formation of a carbonate species, Au_2CO_3^- , which is formed by reaction of CO with Au_2O_2^- . From the carbonate species the reaction can proceed along two branches: (1) dissociation of CO_2 from the carbonate and subsequent reaction of CO with Au_2O^- producing Au_2^- and CO_2 , and (2) reaction of CO with the carbonate species producing simultaneously two CO_2 molecules and Au_2^- . In branch (1) the rate-limiting step is the dissociation of CO_2 from the carbonate requiring an energy of 1.1 eV, while the second step (the reaction

$\text{CO} + \text{Au}_2\text{O}^-$) is barrierless and the formed CO_2 leaves the gold dimer anion spontaneously. Branch (2) involves a reaction barrier of about 0.5 eV for the $\text{CO} + \text{Au}_2\text{CO}_3^-$ reaction, after which the two formed CO_2 molecules detach from the gold dimer spontaneously.

Our investigation of the reactivity and catalytic properties of the gold anion dimer opens new avenues for understanding energetics and pathways of prototype chemical reactions, and produces theoretical predictions awaiting verification by experimental studies.

II. Major Accomplishments

1. Development of a unique molecular dynamics program for simulations of metal-oxide surfaces and interfaces.
2. Development of a computer program for ab-initio molecular dynamics simulations of (heterogeneous) catalytic reactions, and it's use in the first theoretical studies of the catalysis of CO oxidation on small gold clusters supported on magnesia surfaces.
3. Discovery of the role of F-center defects (oxygen vacancies) on metal-oxide surfaces in the catalytic activity of gold nanocatalysts supported on these surfaces. The role of the defects expresses itself in anchoring of the metal clusters (thus inhibiting agglomeration), and in (partial) charging of the adsorbed metal nano-cluster via partial electron transfer from the F-center defect.
4. Discovery of the two-dimensional nature of negatively charged gold clusters (with up to 13 atoms), and it's relation to relativistic corrections to the electronic structure.
5. Elucidation of the electronic structure and structural dynamical fluxionality factors governing and controlling nanocatalytic activity.

III. Technology Transitions

The research achievements resulting from work supported by this grant have been the subject of significant coverage by News and Technological publications, as well invitations to lecture at national and international meetings (see section V).

IV. Supported Personnel

U. Landman, Professor and PI – 10%

DR. Hannu Hakkinen, Senior Research Scientist – 80%

Dr. Bokwon Yoon., Postdoctoral fellow – 25%

Dr. M. Moseler, Postdoctoral fellow – 25%

V. Publications and Presentations

Publications

1. A. Sanchez, S. Abbet, A. U. Heiz, W.-D. Schneider, H. Hakkinen, R. N. Barnett, and U. Landman "When Gold is not Noble: Nanoscale Gold Catalysts", *J. Phys. Chem. A* **103**, 9573 (1999).
2. Hannu Hakkinen and Uzi Landman, "Gold Clusters (Au_N , $2 \leq N \leq 10$) and their Anions", *Phys. Rev B* **62**, R2287 (2000)
3. U. Heiz, S. Abbet, A. Sanchez, W.-D. Schneider, H. Hakkinen, and U. Landman, "Chemical Reactions on Size-Selected Clusters on Surfaces", in *Proceedings of Nobel Symposium 117 on The Physics and Chemistry of Clusters*, held 27 June- 2 July, 2000, in Visby, Sweden (World Scientific, Singapore, 2001), pp. 87-98.
4. S. Abbet, U. Heiz, H. Hakkinen, and U. Landman "CO Oxidation on a Single Pd Atom Supported on Magnesia", *Phys. Rev. Lett.*, **86**, 5950 (2001).

5. Hannu Hakkinen and Uzi Landman, "Gas-Phase Catalytic Oxidation of CO by Au_2 ", *J. Am. Chem. Soc. (Communication)* **123**, 9704 (2001).
6. H. Hakkinen, M. Moseler, U. Landman, "Bonding in Cu, Ag, and Au Clusters: Trends and Surprises", *Phys. Rev. Lett.* **89**, 033401 (2002).7. Hannu Hakkinen, Stephane Abbet, Antonio Sanchez, Ulrich Heiz, Uzi Landman, "Structural, Electronic, and Impurity-Doping Effects in Nanoscale Chemistry: Supported Gold Nanoclusters", in preparation, *Angew. Chem.* (2002).

Invited Talks

(U. Landman, unless noted otherwise)

Invited Speaker, Symposium on "Large-Scale Computations in the Simulations of Materials", Carnegie-Mellon Univ., Pittsburg, March 2000.

Invited Speaker, "Computation Science Workshop", Tsukuba, Japan, March 2000.

Invited Speaker, APS Meeting, Minneapolis, Minnesota, March 2000.

Invited Speaker, "AFOSR Conference on Molecular Dynamics", Boston, May 2000.

Invited Speaker, "12th Annual Workshop on Recent Developments in Electronic Structure Methods – ES2000", Atlanta, May 2000.

Invited Speaker in ASM International Educational Symposium 2000 on "Nanomaterials and Nanotechnology Challenges for the New Millenium: Shaping the World Atom by Atom", Oak Ridge, May 2000.

Plenary Lecturer, Nobel Symposium on "Physics and Chemistry of Clusters", Visby, Sweden, June 2000.

Invited Speaker, (H. Hakkinen) "Cluster Surface Interactions", EURESCO Conference, Castelvecchio Pascoli, Italy, June 2000.

Invited Speaker, "Heterogeneous Catalysis", Lyon, France, July 2000.

Plenary speaker Canada-France-USA Conference on Nanoscience and Technology, Montreal, Canada, October, 2000.

Invited speaker Wright – Patterson Air Force Base, Material Laboratory, Dayton Ohio, December, 2000.

Key note speaker, Annual Dutch Physical Society meeting, Holland, December, 2000.

Invited Speaker "international Conference on Metal Oxide Surfaces", Santa Fe, NM, January, 2001.

Invited Speaker, Special Symposium on Nanoscience and Technology, AAAS Annual Metting, San Francisco, February, 2001.

Distinguished Material Lecture, Pennsylvania State University, College Park, February 2001.

Key note speaker, Seminar on the Future of Nanosclae Science, Stockholm, Sweden, March 2001.

Sackler Symposium of the US National Academy of Science, Nanoscience, Washington, DC, May, 2001.

Invited Speaker, Gordon Research Conference on Clusters and Nanostructures, New London, Connecticut, August, 2001.

Invited Speaker, ACS, Symposium on First Principles Studies of Chemical Dynamic, Chicago, August, 2001.

Invited Speaker (shared with H. Hakkinen), ACS, Symposium on What Can we Really Learn from Clusters About Bulk Behaviour, Chicago, August, 2001

Keynote Speaker, TNT 2001, Trends in Nanotechnology (TNT) Conference. Segovia, Spain, September, 2001..

Plenary speaker, IUPAC conference on Nanoscience and technology, Bangalore, India, February, 2002.

Invited speaker, COST conference on self-assembled nanostructures, Leuven, Belgium, April, 2002.

Plenary speaker, EURESCO conference on Cluster –Surface Interactions and Nanostructures, Granada, Spain, June, 2002.

Plenary Speaker, Nano-7/Ecoss-21, Malmo, Sweden, June, 2002.

Plenary Speaker, Asia SPM4 and Taipei Symposium on Nanotechnology, Taipe, Taiwan, August, 2002

VI. Awards

Uzi Landman received the 2000 Nanotechnology Feynman prize (theoretical), for his pioneering simulations of nanoscale materials systems.
